Supplementary Materials for

Chemical Synthesis and Thermodynamic Characterization of Oxanine-Containing Oligodeoxynucleotides

Seung Pil Pack[1,2], Mitsuru Nonogawa[3], Tsutomu Kodaki[2,3] and Keisuke Makino [1,4]*

[1] International Innovation Center, Kyoto University, Yoshida-honmachi, Sakyo-ku, Kyoto 606-8501, Japan, [2] CREST, JST (Japanese Science and Technology), Kyoto University, Gokasho, Uji 611-0011, Japan, and [3] Institute of Advanced Energy, Kyoto University, Gokasho, Uji 611-0011, Japan.

Figure Legend

Figure S-1. Preparative RP-HPLC separation of the HNO_2-treated dGuo solution. Reaction condition: dGuo; 100 mM, HNO_2 solution; a mixture of $NaNO_2$ (100 mM) and sodium acetate buffer (3.0 M, pH 3.7), temperature; 45°C, time; 4 hr. HPLC condition: mobile phase; sodium phosphate buffer (400 μM, pH 7.4) containing 10% CH_3CN, flow rate; 6 ml/min, column; preparative COSMOSIL C_{18}-PAQ (250 x 28 mm, 5 μm; Nacalai Tesques (Osaka, Japan)).

Figure S-2. RP-HPLC separation of DMT-dOxo and by-product generated from dOxo in the 5'-*O* selective dimethoxytritylation for 3 hr. Rreaction conditions: dOxo, 4-4'-dimethoxytritylchloride, DIEA-Mes and imidazole (the molar ratio being 1: 2: 2: 2). HPLC conditions: mobile phase; 90% aqueous methanol, flow rate; 0.7 ml/min, column; Ultron VX-Nucleotide (150 x 4.6 mm, 5 μm; Shinwa Co. (Kyoto, Japan)).

Figure S-3. ^{1}H NMR (a) and ^{13}C NMR (b) spectra (CD_3CN at 30ºC) of DMT-dOxo-amidite, which was prepared by phosphoramidation of DMT-dOxo using 2-cyanoethyl-*N,N,N',N'*-tetraisopropylphosphoramidite and tetrazole in anhydrous CH_3CN, 3 hr.

Figure S-4. Mass spectroscopy analysis (FAB; m/z 1504 ($M+H^+$)) of 5 mer Oxa-ODN

(5'-GCOAT-3'; $C_{49}H_{61}N_{19}O_{29}P_4$ (theoretical MW: 1503.283318)), synthesized by the method established here. (note : Matrix; glycerin, Inlet; direct, Ion mode; FAB+, Spectrum type; Normal ion [MF-linear], RT; 0.70min, Scan; (2,13), BP ; m/z 102.000, Int.; 1599.98, Output m/z range : 102.000 to 159.9097, Cut level; 0.00%).

Figure S-5. CD spectra data for investigating the base-pair effect of Oxa on whole structure of DNA duplex at 37°C (total concentration of the samples; 16 μM, buffer; 1 M NaCl, 10 mM Na_2HPO_4, 1 mM Na_2EDTA (pH 7.0)). All the CD data were accumulated 10 times and processed through a noise reduction program.

Figure S-6. Linear van't Hoff equation plotting of T_m^{-1} *vs* $\ln(C_t/4)$ for getting thermodynamic parameters, $\Delta H°$ and $\Delta S°$ of DNA duplexes containing O:N base pairs and G:C match.

Figure S-1.

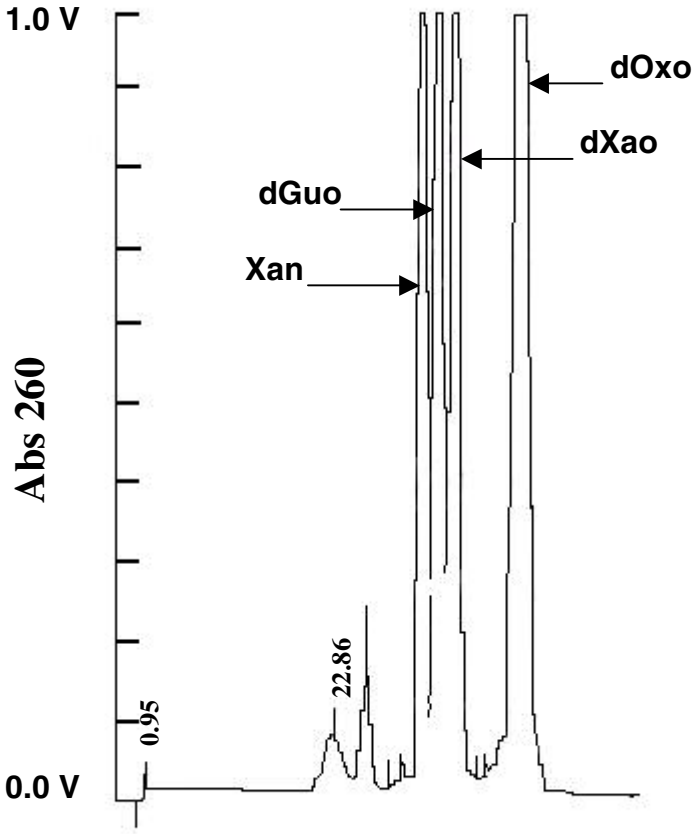


Figure S-2.

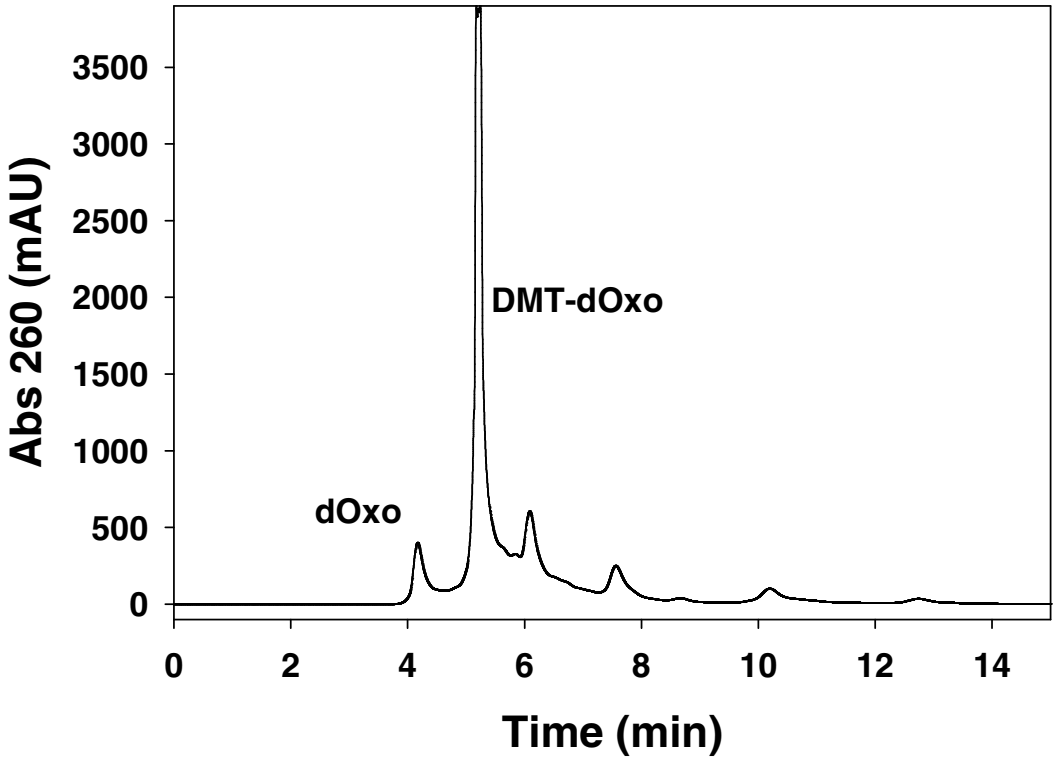

Abs 260 (mAU)
3500
3000
2500
2000
1500
1000
500
0
DMT-dOxo
dOxo
0
2
4
6
8
10
12
14
Time (min)

Figure S-3.

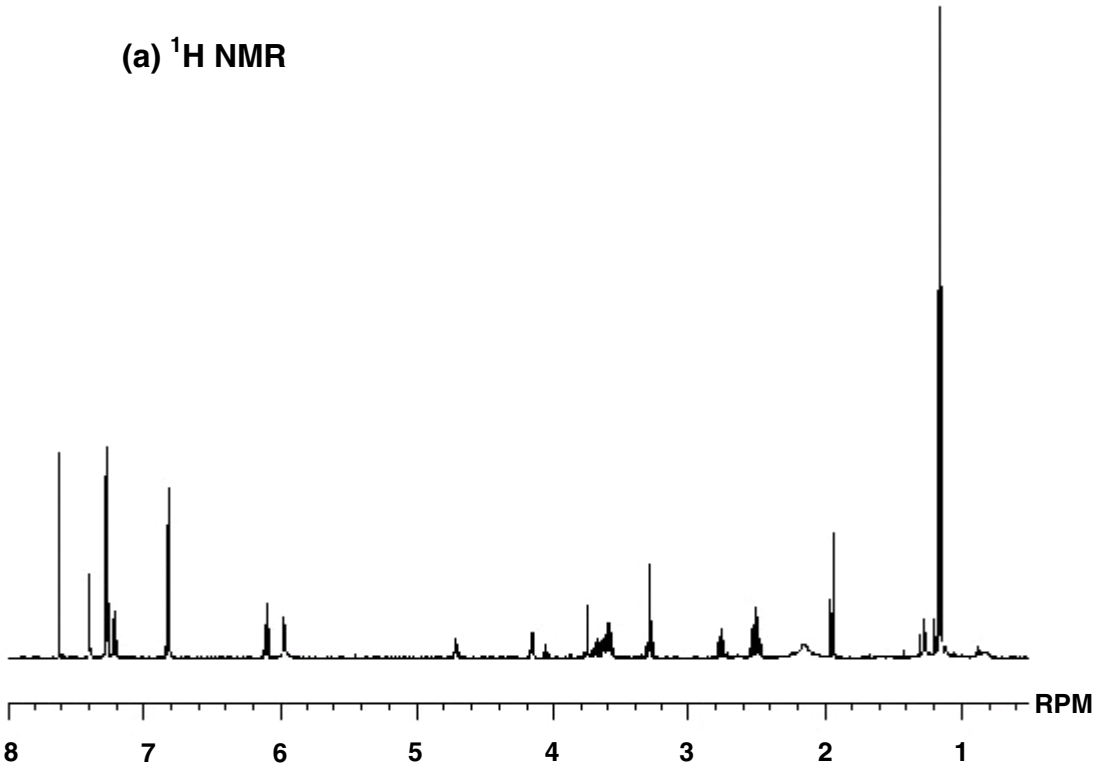


Figure S-3. *(continued)*

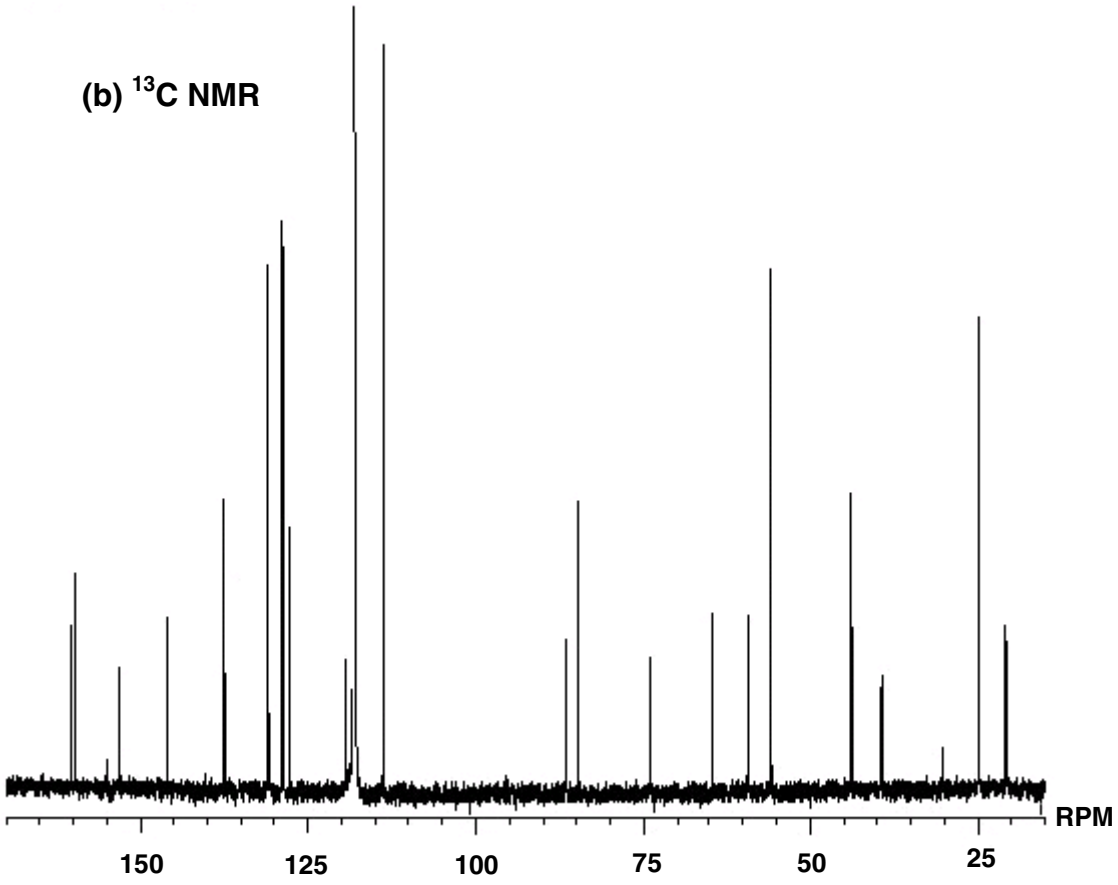


Figure S-4.

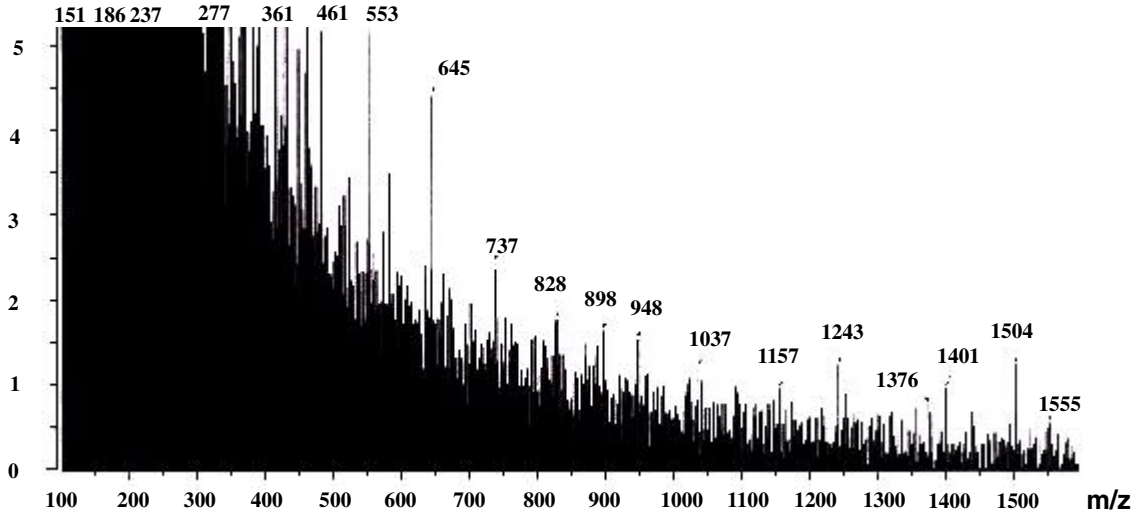

151 186 237
277
361
461
553
645
737
828
898
948
1037
1157
1243
1376
1401
1504
1555
5
4
3
2
1
0
100 200 300 400 500 600 700 800 900 1000 1100 1200 1300 1400 1500
m/z

Figure S-5.

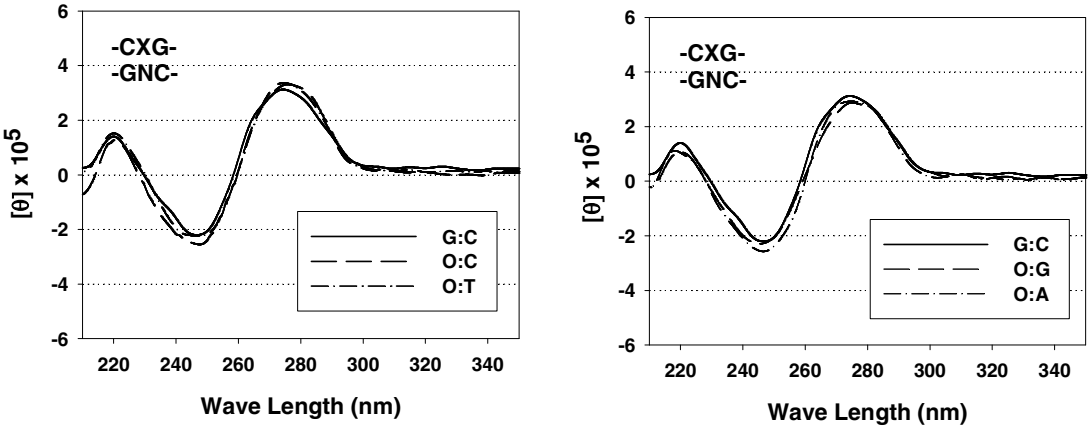
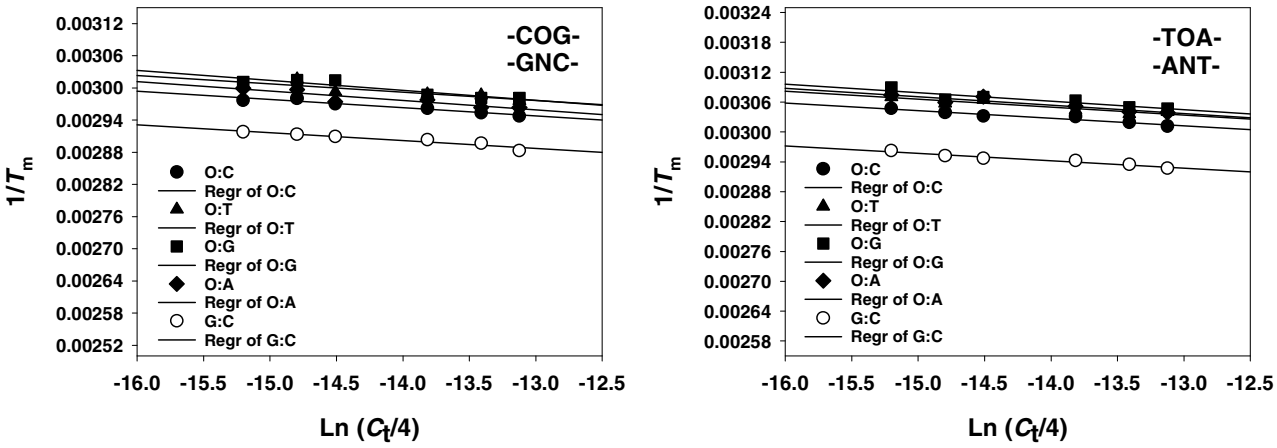

-CXG-
-GNC-
[θ] x 10^5
Wave Length (nm)
G:C
O:C
O:T
-CXG-
-GNC-
[θ] x 10^5
Wave Length (nm)
G:C
O:G
O:A

Figure S-6.


-COG-
-GNC-
1/T_m
Ln (C_t/4)
O:C
Regr of O:C
O:T
Regr of O:T
O:G
Regr of O:G
O:A
Regr of O:A
G:C
Regr of G:C
-TOA-
-ANT-